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Phase equilibria of binary systems of 3-methylthiophene with four different hydrocarbons

Erlin Sapei[a,*], Petri Uusi-Kyyny[a], Kari I. Keskinen[a,b], Ville Alopaeus[a]

[a] *Department of Biotechnology and Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FI-02015 Espoo, HUT, Finland*
[b] *Neste Jacobs Oy, P.O. Box 310, FI-06101 Porvoo, Finland*

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ABSTRACT

Isothermal vapor–liquid equilibrium (VLE) for systems 3-methylthiophene + 2-methylpentane at 333.15 K, 3-methylthiophene + *n*-hexane at 333.15 K, 3-methylthiophene + methylcyclopentane at 343.15 K, and 3-methylthiophene + methylcyclohexane at 373.15 K were measured with a recirculation still. All systems exhibit positive deviation from Raoult's law. No azeotropic behavior was found in any of the systems at the measured temperatures. The experimental results were correlated with the Wilson model and also compared with the original UNIFAC and UNIFAC-Dortmund predictive models. Liquid and vapor-phase composition were determined with gas chromatography. All VLE measurements passed the used thermodynamic consistency tests (integral, infinite dilution and point test). The activity coefficients at infinite dilution are also presented.

1. Introduction

To meet the standards of new environmental legislation and to avoid SO*x* pollution during fuel combustion, ultra-low-sulfur fuel is required by 2010 in many countries [1]. New developments on sulfur separation process designs to further decrease the sulfur level have become one of the major challenges to the refining industry [2]. Design of separation processes to accomplish the removal of sulfur compounds requires the knowledge of the behaviour of sulfur compounds in hydrocarbons. Information of such systems is scarce and experimental work is required.

The major components of gasoline or its blending components originate from Fluid Catalytic Cracking (FCC) unit and contain cycloalkanes in addition to alkanes. Also organic sulfur compounds are present in these refinery streams. 3-Methylthiophene is one of the organic sulfur compounds present in the products [3]. In this work, we measured vapor–liquid equilibrium (VLE) for systems 3-methylthiophene + 2-methylpentane at 333.15 K, 3-methylthiophene + *n*-hexane at 333.15 K, 3-methylthiophene + methylcyclopentane at 343.15 K, and 3-methylthiophene + methylcyclohexane at 373.15 K with a recirculation still. No other VLE data for binaries studied in this work have been found in the literature search. In the previous work, Sapei et al. [4] measured VLE data for systems 3-methylthiophene + 2,2,4-trimethylpentane at 368.15 K, 3-methylthiophene + 2,4,4-trimethyl-1-pentene at 368.15 K, 3-methylthiophene + cyclohexane at 348.15 K, and 3-methylthiophene + 1-hexene at 333.15 K.

2. Experimental

2.1. Materials

3-Methylthiophene, 2-methylpentane, methylcyclopentane, and methylcyclohexane were provided by Sigma–Aldrich, Finland. *o*-Xylene, which was used as a diluent in gas chromatographic analysis, was purchased from Fluka, Finland. The purity of all substances was checked by gas chromatography (GC) equipped with a flame ionization detector (FID). All chemicals were dried over molecular sieves (Merck 3 Å) for 24 h. The refractive indexes, n_D, of the pure liquids were measured at 298.15 K with ABBEMAT-HP automatic refractometer (Dr. Kernchen, Germany) with accuracy ±0.00002. The purity and measured refractive indexes of the chemical used are presented in Table 1. The measured refractive indexes corresponded well with literature values [5].

2.2. Apparatus

The VLE runs were conducted with a circulation still of the Yerazunis-type [6] built at the glass workshop of Helsinki University of Technology with minor modifications to the original design

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* Corresponding author. Tel.: +358 9 4512638; fax: +358 9 451 2694.
E-mail address: sapei@cc.hut.fi (E. Sapei).

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Table 1
Purity and refractive indexes (n_D) of pure components.

Component	GC purity (mass %)	n_D (298.15 K)	
		Experimental	Literature [5]
3-Methylthiophene	99.78	1.5172	1.5176
2-Methylpentane	99.98	1.3685	1.3687
n-Hexane	99.99	1.3724	1.3723
Methylcyclopentane	99.75	1.4067	1.4070
Methylcyclohexane	99.97	1.4025	1.4026
o-Xylene (used as diluent)	99.99	1.5028	1.5029

[7]. Experimental setup is described in detail in the previous works [7,8]. Approximately 80 ml of reagents were needed to run each measurement.

Temperatures were measured with a Pt-100 resistance temperature probe, which was located at the bottom of the packed section of the equilibrium chamber and connected to Thermometer (F200, Tempcontrol) which has a manufacturer's stated accuracy of ±0.02 K and the calibration uncertainty was ±0.01 K. The uncertainty of the whole temperature measurement system is estimated to be ±0.05 K.

Pressure was measured with a Druck pressure transducer PMP 4070 (0–100 kPa) connected to a Red Lion panel meter. The inaccuracy of the instruments was reported to be ±0.07 kPa by the manufacturer. The pressure measurement system was calibrated against BEAMEX PC 105-1166 pressure calibrator. The uncertainty of the whole pressure measurement system including the calibration uncertainty is expected to be less than ±0.17 kPa.

In order to improve mixing in the sampling chambers and mixing chamber of the condensed vapor phase and the liquid phase, DC electric motors (Graupner speed 400) were equipped with magnetic stirrer bars, which deliver stirring action in the chambers.

2.3. Experimental procedures

Pure component 1 was introduced in the recirculation still and its vapor pressure was measured at several temperatures. Then component 2 was introduced into the recirculation still. It took approximately from 30 min to 45 min to achieve constant temperature. The temperature was held constant for approximately 30–45 min before sampling.

After equilibration, the temperature in the equilibrium cell was measured and then vapor and liquid samples were withdrawn with a 1 ml Hamilton Sample Lock syringe and after that injected into the cooled 2 ml auto sampler vial containing approximately 1 ml *o*-xylene (as diluent). The compositions of both samples were immediately measured by gas chromatography (GC). To prevent spreading of the unpleasant odor of the sulfur compounds, the GC was placed in a closed and ventilated cupboard.

2.4. Analysis and GC calibration

The liquid and vapor samples were analyzed with a Agilent 6850A gas chromatograph equipped with an auto sampler and a FID. The GC-column used was a HP-1 Dimethylpolysiloxane (60.0 m × 250 μm × 1.0 μm). The injector and FID were set at 250 °C. Helium was used as the carrier gas at a constant flow rate of 1 ml min^{-1} and inlet split ratio 100:1. The initial oven temperature was held at 70 °C for 2 min and then increased subsequently to 150 °C at rate of 8 °C min^{-1} and was held at 150 °C for 3 min. The total run time was 15 min.

The pure components were used to determine the retention times, after that the GC was calibrated with 15 mixtures of known composition that were prepared gravimetrically. To reduce the volume of the sample, *o*-xylene was used as solvent.

The response factor of component 2 (F_2) was calculated from Eq. (1):

$$\frac{m_2}{m_1}\frac{A_1}{A_2} = F_2 \tag{1}$$

Therefore, the vapor or liquid composition of component 1 can be calculated from:

$$x_1 = \frac{A_1/M_1}{A_1/M_1 + \left(F_2(A_2/M_2)\right)} \tag{2}$$

where A_1 and A_2 are the GC peak areas, M_1 and M_2 are the molar masses, and m_1 and m_2 were masses in the gravimetrically prepared sample of components 1 and 2, respectively. The maximum error of liquid and vapor composition measurements is estimated to be 0.003 mole fraction.

Table 2
Critical temperature (T_c), critical pressure (P_c), acentric factor (ω), liquid molar volume (V_i) at 298.15 K, pure component vapor pressure equation parameters (A, B, and C) for the Antoine equation, recommended temperature range of the vapor pressure correlation (T_{min} and T_{max}).

Component	3-Methylthiophene	2-Methylpentane	*n*-Hexane	Methyl cyclopentane	Methyl cyclohexane
T_c[a] (K)	615.00	497.5	507.43	532.79	572.19
P_c[a] (MPa)	4.950	3.010	3.012	3.785	3.471
ω[a]	0.242	0.278	0.305	0.230	0.235
V_i[a] (cm^3 mol^{-1})	96.585	132.931	131.306	113.042	128.192
A[b]	6.7218[c]	7.532[e]	6.980[d]	6.881[e]	6.909[e]
B[b]	2886.0131[c]	2998.063[e]	2724.960[d]	2731.000[e]	2998.940[e]
C[b]	−68.3674[c]	−28.016[e]	−47.736[d]	−47.099[e]	−47.914[e]
T_{min} (K)	333.15	290.34	307.31	300.40	325.39
T_{max} (K)	387.89	333.37	342.00	345.10	373.90
$\lvert\Delta P_{aver}\rvert$[f] (kPa)	0.19	0.03	0.01	0.09	0.09
$\lvert\Delta P_{aver}\rvert$[g] (kPa)	0.16	0.22	0.41	0.11	0.12

[a] Ref. [5].
[b] P^S (MPa) = exp($A - [B/(T/K + C)]$).
[c] Ref. [4].
[d] Ref. [9].
[e] This work.
[f] $\left|\Delta P_{aver}\right| = \frac{\sum_{i=1}^{N_{VLE}}\left|P_{i,measured} - P_{i,calculated}\right|}{N_{VLE}}$.
[g] $\left|\Delta P_{aver}\right| = \frac{\sum_{i=1}^{N_{VLE}}\left|P_{i,measured} - P_{i,literature}\right|}{N_{VLE}}$